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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Water-Dilutable Two-Component Coating Composition

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Notice: This application is as filed and may therefore contain an  
incomplete specification.



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**Abstract of the Disclosure**

**A water-dilutable, two-component coating composition is disclosed that contains**

- (a) a polyisocyanate component composed of one or more organic polyisocyanates, and**
- (b) an aqueous polyurethane dispersion prepared by radical-initiated polymerization of polyurethane macromonomers containing carboxyl, phosphono or sulfo groups, lateral and/or terminal vinyl groups, and, if desired, hydroxyl, urethane, thiourethane and/or urea groups.**

## WATER-DILUTABLE TWO-COMPONENT COATING COMPOSITION

Background of the Invention

The present invention relates to a water-dilutable, two-component coating composition.

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Summary of the Invention

It is an object of the present invention to provide a water-dilutable, two-component coating composition.

10 These and other objects according to the invention are provided by a water-dilutable, two-component coating composition that comprises:

- (a) a polyisocyanate component that contains at least one organic polyisocyanate, and
- (b) an aqueous polyurethane dispersion prepared by radical-initiated polymerization of  
15 polyurethane macromonomers that contain:
  - at least one carboxyl, phosphono or sulfo group,
  - at least one vinyl group, which group  
20 may be a lateral group or a terminal group, and
  - optionally at least one hydroxyl, urethane, thiourethane or urea group.

25 In one embodiment, the aqueous polyurethane dispersion (b) is prepared by producing a urethane macromonomer by radical-initiated polymerization of (A) one or more polyhydroxy compounds selected from the group consisting of (A1) polyhydroxy-polyethers, (A2) polyhydroxy-polyesters, and (A3) polyhydroxy-polycarbonates, and, optionally (A4) low molecular  
30

weight polyols, (B) one or more polyisocyanates, (C) one or more vinyl monomers that contain at least one vinyl group, selected from the group consisting of (C1) vinyl monomers that contain one group which is reactive toward isocyanate groups, which group is selected from an amino, hydroxyl and mercapto group, (C2) vinyl monomers that contain at least two groups which are reactive toward isocyanate groups, selected as defined in (C1), it being possible for the vinyl monomers (C1) and (C2), if desired, to be employed in a mixture, (D) polyhydroxy compounds that contain at least one acid group selected from a carboxyl, sulfo and phosphono group, and, optionally, (D') acid-group-containing polyamines, polythiols or amino alcohols or amino thiols, the acid groups of which are as defined in (D), and reacting the urethane macromonomer with at least one alcohol, amine or thiol, wherein the resulting polyurethane contains acid groups, terminal hydroxyl groups and vinyl groups, which vinyl groups may be terminal or lateral vinyl groups.

The another embodiment, the urethane macromonomer is prepared in the presence of a vinyl compound (E) or in the presence of a mixture of two or more vinyl compounds (E), the vinyl compounds (E) being selected from the group consisting of:

- esters of olefinically unsaturated mono- or polycarboxylic acids with mono- or polyhydric (cyclo)aliphatic, aromatic or mixed aliphatic-aromatic alcohols having 1 to 15 carbon atoms,
- amides or nitriles of the above-defined carboxylic acids, which in the case of

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- the amides optionally may be substituted on the nitrogen atom,
- esters of mono- or polyhydric, olefinically-unsaturated alcohols with (cyclo)aliphatic, aromatic or mixed aliphatic-aromatic carboxylic acids that have 2 to 15 carbon atoms,
  - olefinically-unsaturated aldehydes and ketones,
  - ethers of mono- or polyhydric, olefinically-unsaturated alcohols with (cyclo)aliphatic, aromatic or mixed aliphatic-aromatic alcohols that have 1 to 15 carbon atoms,
  - vinyl and vinylidene halides, and
  - vinyl aromatic compounds.

In yet another embodiment, the aqueous polyurethane dispersion (b) is prepared by radical-initiated polymerization in a mixture of water and an organic solvent which is inert toward isocyanate groups, optionally in the presence of unsaturated monomers (E) which are copolymerizable with the polyurethane macromonomers, and optionally with removal of the organic solvent by distillation before or after the free-radical polymerization.

In still another embodiment, the aqueous polyurethane dispersion (b) is prepared by radical-initiated polymerization in an unsaturated monomer (E) which serves as solvent and is copolymerizable with the polyurethane macromonomers, optionally in the presence of further copolymerizable unsaturated monomers (E).

The objects of the invention also are provided by a process for the preparation of a water-dilutable two-component coating composition, wherein prior to the polymerization of the urethane macromonomers, at least one vinyl monomer is added which carries at least one functional group selected from the group consisting of carboxyl, hydroxyl, amino, ether and mercapto groups. The unsaturated monomer (E) may be added before or during polymerization but after the synthesis of the urethane macromonomer.

The invention also provides a coating method, comprising the steps of providing a substrate, and coating a layer of a composition according to the invention on the substrate. In a preferred embodiment, the substrate is a metallic substrate.

Other objects, features and advantages of the present invention will become apparent from the following detailed description. It should be understood, however, that the detailed description and the specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

#### Description of the Preferred Embodiments

A coating composition according to the invention comprises

(a) a polyisocyanate component composed of one or more organic polyisocyanates, and

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(b) an aqueous polyurethane dispersion prepared by radical-initiated polymerization of polyurethane macromonomers that contain carboxyl, phosphono or sulfo groups, lateral and/or terminal vinyl groups, and, if desired, hydroxyl, urethane, thiourethane and/or urea groups.

Polyisocyanate component (a) may be any of the organic polyisocyanates which are liquid at room temperature and which have free isocyanate groups attached to aliphatic, cycloaliphatic, araliphatic and/or aromatic structures. Polyisocyanate component (a) generally has a viscosity at 23°C of from 1 to 20,000 mPa.s. Polyisocyanate component (a) particularly preferably comprises polyisocyanates or mixtures of polyisocyanates which have isocyanate groups attached exclusively to aliphatic and/or cycloaliphatic structures and which have an (average) NCO functionality of between 2.0 and 5.0.

If required, the polyisocyanates can be employed as a mixture with small quantities of inert solvents, in order to reduce the viscosity to a level within the specified ranges. The quantity of such solvents, however, is generally calculated so that the coating compositions according to the invention which are ultimately obtained contain not more than 30% by weight of solvent, this calculation including any solvents which may still be present in the polymer dispersions or solutions. Examples of solvents which are suitable as additives for the polyisocyanates are aromatic hydrocarbons such as "solvent naphtha," or else aprotic solvents such as aliphatic ethers, (e.g., diethylene glycol dimethyl

ether, dipropylene glycol dimethyl ether), glycol ether esters, or amides such as N-methylpyrrolidone or dimethylformamide.

5 Polyisocyanates suitable as component (a) are diisocyanates, particularly the so-called paint polyisocyanates that contain isocyanate groups attached to aromatic or (cyclo)aliphatic structures, the latter aliphatic polyisocyanates being particularly preferred.

10 The diisocyanates are the compounds which are known in the polyurethane and paints sector, such as aliphatic, cycloaliphatic or aromatic diisocyanates. These preferably possess the formula  $Q(NCO)_2$ , where Q is a hydrocarbon radical that has 4 to 40 carbon atoms, in particular 4 to 20 carbon atoms, and is preferably an aliphatic hydrocarbon radical that has 4 to 12 carbon atoms, a cycloaliphatic hydrocarbon radical that has 6 to 15 carbon atoms, an aromatic hydrocarbon radical having 6 to 15 carbon atoms or  
15 an araliphatic hydrocarbon radical that has 7 to 15 carbon atoms.

Examples of preferred diisocyanates include tetramethylene diisocyanate, hexamethylene diisocyanate, dodecamethylene diisocyanate,  
25 1,4-diisocyanatocyclohexane, 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (isophorone diisocyanate), 4,4'-diisocyanatodicyclohexylmethane, 4',4''-diisocyanato-2,2-dicyclohexylpropane, 1,4-diisocyanatobenzene, 2,4- or  
30 2,6-diisocyanatotoluene or mixtures of these isomers, 4,4'- or 2,4'-diisocyanatodiphenylmethane, 4',4''-diisocyanato-2,2-diphenylpropane, p-xylylene diisocyanate and  $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-m- or



-p-xylylene diisocyanate, and mixtures of these compounds.

Other suitable polyisocyanates are those which contain heteroatoms in the radical which links the isocyanate groups. Examples of these are polyisocyanates which have carbodiimide groups, allophanate groups, isocyanurate groups, urethane groups, acylated urea groups or biuret groups. With regard to other suitable polyisocyanates reference is made, for example, to DE-A 29 28 552.

Examples of polyisocyanates that are highly suitable include paint polyisocyanates based on hexamethylene diisocyanates,  $\alpha, \alpha, \alpha', \alpha'$ -tetramethyl-m- and -p-xylylene diisocyanate (TMXDI) or on 1-isocyanato-3,3,5-trimethyl-4-isocyanatomethylcyclohexane (IPDI) and/or bis(isocyanatocyclohexyl)methane, especially polyisocyanates that are based solely on hexamethylene diisocyanate. Paint polyisocyanates based on these diisocyanates should be understood as including known derivatives of these diisocyanates which possess biuret, urethane, uretdione and/or isocyanurate groups. Subsequent to their preparation, these have been freed from excess starting diisocyanate as required in a known manner, preferably by distillation, down to a residual content of less than 0.5% by weight. The preferred aliphatic polyisocyanates to be used in accordance with the invention include polyisocyanates which meet the above mentioned criteria, contain biuret groups and are based on hexamethylene diisocyanate. These can be obtained, for example, by the processes of US-A-3,124,605, 3,358,010, 3,903,126, 3,903,127

or 3,976,622, and comprise mixtures of N,N,N-tris(6-isocyanatohexyl)biuret with minor quantities of its higher homologs. Other preferred aliphatic polyisocyanates are the cyclic trimers of hexamethylene diisocyanate which conform to the above mentioned criteria. These can be obtained in accordance with US-A-4,324,879 and essentially comprise N,N,N-tris(6-isocyanatohexyl) isocyanurate in a mixture with minor quantities of its higher homologs. Particular preference is given to mixtures, conforming to the above mentioned criteria, of polyisocyanates which are based on hexamethylene diisocyanate and which possess uretdione and/or isocyanurate groups. These mixtures are formed by catalytic oligomerization of hexamethylene diisocyanate using trialkylphosphines. Particular preference is given to the last-mentioned mixtures having a viscosity at 23°C of from 1 to 20,000 mPa.s and having an NCO functionality of between 2.0 and 5.0.

In the context of the present invention it is advantageous also to employ polyisocyanates which are dispersible in water, such as those described, for example, in EP-B-0 061 628, EP-B-0 206 059 and EP-B-0 469 389. Such polyisocyanates contain additional hydrophilic groups which may be nonionic, e.g., polyoxyalkylene groups, or ionic, preferably anionic groups, for example, groups derived from carboxylic, sulfonic or phosphonic acids.

Aromatic polyisocyanates are also suitable, but are less preferred. Preferred aromatic polyisocyanates are paint polyisocyanates based on 2,4-diisocyanatotoluene or its technical-grade

mixtures with 2,6-diisocyanatotoluene, or based on 4,4-diisocyanatodiphenylmethane or its mixtures with its isomers and/or higher homologs. Examples of such aromatic paint polyisocyanates are the isocyanates that possess urethane groups, such as those obtained by reaction of excess quantities of 2,4-diisocyanatotoluene with a polyhydric alcohol such as trimethylol propane, followed possibly by removal by distillation of the unreacted diisocyanate excess. Examples of other aromatic paint polyisocyanates are the trimers of the monomeric diisocyanates mentioned, i.e., the corresponding isocyanato-isocyanurates, which may subsequent to their preparation have been freed, preferably by distillation, from excess monomeric diisocyanates. Polyisocyanate component (a) also may comprise any desired mixtures of the polyisocyanates mentioned.

The polyurethane dispersions (b) are described in DE-A-41 22 266, DE-A-41 22 265 and EP-A-0 098 752. The polyurethane macromonomers required for their preparation are prepared by polyaddition of polyhydroxy compounds (A) from the group consisting of polyhydroxy-polyethers (A1), polyhydroxy-polyesters (A2) and polyhydroxy-polycarbonates (A3), if desired in combination with low molecular weight compounds (A4) which possess two or more functional groups selected in each case from among hydroxyl, amino and mercapto groups; polyisocyanates (B); monomers (C) that have at least one vinyl group and that contain one (C1) or at least two (C2) groups which are reactive toward isocyanate, such as amino, mercapto or, preferably,

hydroxyl groups; and also polyhydroxy compounds (D) which contain acid groups, such as polyhydroxycarboxylic acids, polyhydroxyphosphonic acids or polyhydroxysulfonic acids, and/or, if desired,  
 5 acid group-containing polyamines or polythiols (D').

The polyhydroxy compounds A are selected from the groups consisting of the polyhydroxy-polyethers (A1), namely compounds of the formula



10 in which

R is hydrogen or a lower alkyl radical, with various substituents if desired,

n is a number from 2 to 6 and

m is a number from 10 to 120.

15 Examples are poly(oxytetramethylene) glycols, poly(oxyethylene) glycols and poly(oxypropylene) glycols. The preferred polyhydroxy-polyethers are poly(oxypropylene) glycols having a molar mass in the range from 400 to 5000 g/mol.

20 The polyhydroxy-polyesters (A2) are prepared by esterification of organic polycarboxylic acids or their anhydrides with organic polyols. The polycarboxylic acids and the polyols may be aliphatic or aromatic polycarboxylic acids and  
 25 polyols.

The polyols used for the preparation include alkylene glycols such as ethylene glycol, butylene glycol, 1,6-hexanediol, neopentyl glycol and other glycols, for example, dimethylolcyclohexane,  
 30 2,2-bis(4-hydroxycyclohexyl)propane and also trishydroxyalkylalkanes such as e.g.

trimethylolpropane, and tetrakis(hydroxyalkyl)alkanes such as pentaerythritol.

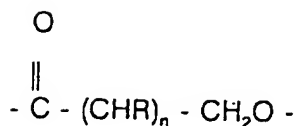
5       The acid component of the polyester principally comprises low molecular weight polycarboxylic acids or their anhydrides that have 2 to 18 carbon atoms in the molecule. Examples of suitable acids are phthalic acid, isophthalic acid, terephthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, succinic acid, adipic acid, 10       azelaic acid, sebacic acid, maleic acid, glutaric acid, hexachloroheptanedicarboxylic acid, alkyl- and alkenylsuccinic acids such as n-octenylsuccinic acid and n- or iso-dodecenylsuccinic acid, tetrachlorophthalic acid, trimellitic acid and 15       pyromellitic acid. In place of these acids it is also possible to use their anhydrides where they exist. Dimeric and trimeric fatty acids can also be employed as polycarboxylic acids.

20       The terms polyhydroxy-polyether and polyhydroxy-polyester also refer to those products of this kind which contain monomers with carboxylate, phosphonate or sulfonate groups.

25       It also is possible to use polyhydroxy-polyesters which are derived from lactones. These products are obtained, for example, by reacting an  $\epsilon$ -caprolactone with polyols. Such products are described in US-A-3,169,945.

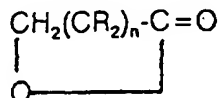
30       The polylactone-polyols obtained by this reaction are distinguished by the presence of a terminal hydroxyl group and by recurring polyester units derived from the lactone. These recurring units in the molecule may conform to the formula

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in which n is preferably from 4 to 6 and the substituent R is hydrogen, an alkyl radical, a cycloalkyl radical or an alkoxy radical, with the proviso that no substituent contains more than 12 carbon atoms.

The lactone used as starting material may be any desired lactone or combination of lactones, provided said lactone contains at least 6 carbon atoms in the ring, for example, 6 to 8 carbon atoms, and provided at least 2 hydrogen substituents are present on the carbon atom attached to the oxygen group of the ring. The lactone used as starting material can be represented by the following formula:



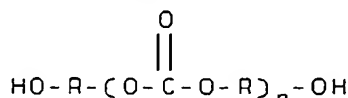
in which n and R are as already defined.

The preferred lactones are the  $\epsilon$ -caprolactones, in which n has the value 4. The most preferred lactone is unsubstituted  $\epsilon$ -caprolactone, in which n has the value 4 and all substituents R are hydrogen. This lactone is particularly preferred since it is available in large quantities and gives coatings having excellent

properties. Various other lactones may be used individually or in combination.

Examples of aliphatic polyols which are suitable for reaction with the lactone are ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, dimethylolcyclohexane, trimethylolpropane and pentaerythritol.

Polyhydroxy-polycarbonates (A3) include polycarbonate-polyols and polycarbonate-diols, conforming to the formula



in which R is an alkylene radical and n denotes an integer from 10 to 120. These OH functional polycarbonates can be prepared by reacting polyols such as 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol, triethylene glycol, 1,4-bis(hydroxymethyl)-cyclohexane, 2,2-bis(4-hydroxycyclohexyl)propane, neopentyl glycol, trimethylolpropane or pentaerythritol with dicarbonates such as dimethyl, diethyl or diphenyl carbonate or phosgene. Mixtures of such polyols can also be employed.

The above-described polyhydroxy-polyethers, polyhydroxy-polyesters and polyhydroxy-polycarbonates can also be employed together. Furthermore, these polyhydroxy compounds may also be employed together with different quantities of low molecular weight, isocyanate-reactive polyols, polyamines or polythiols (A4). Examples of suitable compounds of this kind are ethylene glycol,

butanediol, pentaerythritol, trimethylolpropane, ethylene diamine, propylenediamine, hexamethylenediamine,  $\beta$ -mercaptoethanol and  $\beta$ -aminoethanol.

5           The monomers (C) contain at least one vinyl group. They include monomers (C1) that contain one group reactive toward isocyanate, such as amino, mercapto or hydroxyl groups, preferably hydroxyl groups, and monomers (C2) that contain at least two  
10           groups reactive toward isocyanate, such as amino, mercapto or hydroxyl groups, preferably hydroxyl groups.

          Examples of the monomers (C1) are the hydroxyalkyl(meth)acrylates such as hydroxyethyl and  
15           hydroxypropyl (meth)acrylate, the reaction products of monoepoxides and  $\alpha,\beta$ -unsaturated carboxylic acids, such as reaction products of Versatic acid glycidyl esters and (meth)acrylic acid or of  
20            $\alpha,\beta$ -unsaturated glycidyl esters and monocarboxylic acids, for example, reaction products of glycidyl (meth)acrylate and stearic acid or linseed oil fatty acid, and finally, for example, acrylic monomers which contain amino or mercapto groups, for example, t-butylaminoethyl (meth)acrylate.

25           Examples of monomers (C2) are di- and poly-hydroxyvinyl compounds such as allyl or vinyl ethers of polyhydric alcohols or phenols, for example, trimethylolpropane monovinyl ether, trimethylol propane monoallyl ether, pentaerythritol  
30           monovinyl or monoallyl ether, esters of polyhydric alcohols with unsaturated carboxylic acids, for example, trimethylolpropane mono(meth)acrylate or glycerol mono(meth)acrylate, adducts of



$\alpha,\beta$ -unsaturated carboxylic acids such as (meth)acrylic acid, itaconic acid or vinylacetic acid with diepoxides, for example, bisphenol A diglycidyl ether or hexanediol diglycidyl ether, and  
5 adducts of dicarboxylic acids, such as adipic acid or terephthalic acid with glycidyl (meth)acrylates. Appropriate vinyl compounds containing two or more amino or mercapto groups are derived, for example, from polyamines and unsaturated carboxylic acids,  
10 from N-vinyl polyamines or, for example, from unsaturated polycarboxylic acids which are esterified with 2-mercaptopropanol, such as bis-2-mercaptopropyl maleate.

A further component employed for preparation  
15 of the polyurethane dispersions comprises low molecular weight polyols (D), preferably diols, which also contain an ionic group in the form of a carboxyl, phosphono or sulfo group. Examples of this group of monomers are  
20  $\alpha$ -C<sub>2</sub>-C<sub>10</sub>-bishydroxycarboxylic acids, such as dihydroxypropionic acid, dimethylolpropionic acid, dihydroxyethylpropionic acid, dimethylolbutyric acid, dihydroxysuccinic acid, dihydroxybenzoic acid or 3-hydroxy-2-hydroxymethylpropanesulfonic acid or  
25 1,4-dihydroxybutanesulfonic acid. The components (D') are analogous polyamines and polythiols (preferably diamines and dithiols) containing acid groups, for example, diaminobenzoic acid, lysine, dimercaptosuccinic acid and dimercap-  
30 topropanesulfonic acid.

Prior to their reaction, these monomers can be neutralized with a tertiary amine, such as trimethylamine, triethylamine, dimethylaniline,

diethylaniline or triphenylamine, in order to avoid a reaction of the acid group with the isocyanate. If the probability of such a reaction is only small, it is also possible for the acid groups not to be neutralized until after their incorporation into the polyurethane macromonomer. In this case, neutralization is carried out with aqueous solutions of alkali metal hydroxides or with amines, for example, with trimethylamine, triethylamine, dimethylaniline, diethylaniline, triphenylamine, dimethylethanolamine, aminoethylpropanol, dimethylaminomethylpropanol, dimethylisopropanolamine or with ammonia. In addition, the neutralization can also be undertaken with mixtures of amines and ammonia.

Examples of suitable polyisocyanates (B) are trimethylene diisocyanate, tetramethylene diisocyanate, pentamethylene diisocyanate, hexamethylene diisocyanate, propylene diisocyanate, ethylene diisocyanate, 2,3-dimethylbutylene diisocyanate, 1-methyltrimethylene diisocyanate, 1,3-cyclopentylene diisocyanate, 1,4-cyclohexylene diisocyanate, 1,2-cyclohexylene diisocyanate, 1,3-phenylene diisocyanate, 1,4-phenylene diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 4,4'-biphenylene diisocyanate, 1,5-naphthylene diisocyanate, 1,4-naphthylene diisocyanate, 1-isocyanatomethyl-5-isocyanato-1,3,3-trimethylcyclohexane, bis(4-isocyanatocyclohexyl)-methane, bis(4-isocyanatophenyl)methane, 4,4'-diisocyanatodiphenyl ether, 2,3-bis(8-isocyanatooctyl)-4-octyl-5-hexylcyclohe-

xene, tetramethylxylylene diisocyanates, trimethylhexamethylene diisocyanates, isocyanurates of the above diisocyanates, or allophanates of the above diisocyanates. Mixtures of polyisocyanates  
5 can also be employed.

It is particularly important for the polyurethane dispersions (b) that the macromonomers which lead to these dispersions contain terminal and/or lateral vinyl groups. The term "terminal  
10 vinyl groups" refers to those vinyl groups which are pendant at the beginning or the end of the polymer chain. The term "lateral vinyl groups" denotes vinyl groups which are not pendant at the beginning or end of a polymer chain. The incorporation of  
15 terminal vinyl groups is carried out by reacting a prepolymer obtained by reaction of the polyols (A) and the polyhydroxycarboxylic, polyhydroxyphosphonic or polyhydroxysulfonic acids (D) with the polyisocyanate (B), which contains free isocyanate  
20 groups, with a vinyl monomer (C) of the above mentioned type (C1) containing a group which is reactive toward isocyanate groups.

The incorporation of lateral vinyl groups is carried out by addition of vinyl monomers (C2) that  
25 contain at least two groups which are reactive toward isocyanate as well as at least one vinyl group.

In this context the monomers (C2) either can be added directly to the polyhydroxy compounds (A)  
30 prior to reaction with polyisocyanate (B) or they can be reacted, in a separate reaction step involving chain extension, with an isocyanato-functional urethane macromonomer.

The macromonomers synthesized from these monomers additionally may be modified by the incorporation of amines, alcohols and/or thioalcohols. For this purpose the initially-produced intermediate, that contains terminal isocyanate radicals, is not reacted solely with the vinyl monomer (C), but rather this monomer is reacted together with amines, alcohols and/or thioalcohols. Examples of compounds which are suitable in this respect are primary amines such as propylamine, butylamine, pentylamine, 2-amino-2-methylpropanol, ethanolamine and propanolamine; secondary amines such as diethanolamine, dibutylamine and diisopropanolamine; primary alcohols such as methanol, ethanol, propanol, butanol, hexanol, dodecanol and stearyl alcohol; secondary alcohols such as isopropanol and isobutanol, and the corresponding thioalcohols.

The preparation of the intermediates in the first steps is carried out by the conventional methods as are known in urethane chemistry. In these methods the catalysts employed may be tertiary amines such as triethylamine, dimethylbenzylamine and diazabicyclooctane, and also dialkyltin(IV) compounds, such as dibutyltin dilaurate, dibutyltin dichloride and dimethyltin dilaurate. The reaction takes place without solvent in the melt, in the presence of a solvent, or in the presence of a so-called reactive diluent, as disclosed below. Suitable solvents are those that can later be removed by distillation, examples being dioxane, methyl ethyl ketone, methyl isobutyl ketone, acetone, tetrahydrofuran, toluene and xylene. These

solvents can be distilled off in whole or in part after the preparation of the polyurethane macromonomers or after the free-radical polymerization. In addition, the reaction also can be carried out in a high-boiling, water-dilutable solvent, for example, in N-methylpyrrolidone, which then remains in the dispersion. Prior to the process of dispersion it is also possible to add further solvents such as glyco ethers and their esters. Examples of suitable glycol ethers are butylglycol, butyldiglycol, methoxypropanol, dipropylene glycol monomethyl ether or diglycol dimethyl ether. The reactive diluents (E) are  $\alpha,\beta$ -unsaturated monomers which, in the final stage, are copolymerized with the macromonomers that contain vinyl groups. Examples of such reactive diluents are  $\alpha,\beta$ -unsaturated vinyl monomers such as alkyl acrylates, alkyl methacrylates and alkyl crotonates, that have 1 to 20 carbon atoms in the alkyl radical, di-, tri- and tetraacrylates, methacrylates and crotonates of glycols, tri- and tetrafunctional alcohols, substituted and unsubstituted acrylamides and methacrylamides, vinyl ethers,  $\alpha,\beta$ -unsaturated aldehydes and ketones, vinyl alkyl ketones that have 1 to 20 carbon atoms in the alkyl radical, vinyl ethers, vinyl esters, diesters of  $\alpha,\beta$ -unsaturated dicarboxylic acids, styrene and styrene derivatives, such as  $\alpha$ -methylstyrene.

The polyurethane macromonomers can be prepared by a variety of routes. The first method of preparation entails reaction of polyhydroxy compounds (A) with polyisocyanates (B) under the conditions specified in the previous paragraph. The

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further monomers, namely the polyhydroxy acids (D) or the polyamino or polymercapto acids (D') and the vinyl monomers (C2) which carry at least two groups which are reactive toward isocyanate, are added to the monomer (A) from the start. In this context, the proportions of the reactants, especially the polyisocyanate, are chosen so that a macromonomer having terminal hydroxyl groups is produced. This macromonomer, which additionally contains carboxyl, phosphono or sulfo groups and lateral vinyl groups, is transferred to an aqueous dispersion. It is then polymerized via the vinyl groups, using free-radical initiators, to form the polyurethane dispersion, the polyurethane in this case still containing hydroxyl groups.

A second method of preparation corresponds to the first procedure except that the proportions are chosen so that a macromonomer that has terminal isocyanate groups is produced. In addition, this macromonomer also contains carboxyl, phosphono or sulfo groups and lateral vinyl groups. The free isocyanate groups of this macromonomer then are reacted with primary or secondary amines, alcohols or thioalcohols to form urea, urethane or thiourethane groups. The macromonomer thus modified is then likewise polymerized via the vinyl groups using free-radical initiators.

A third method of preparation is analogous to the second method, except that the free isocyanate groups of the macromonomer are reacted with a vinyl monomer (C1) which carries a group which is reactive toward isocyanate, if desired in a mixture with primary or secondary amines, alcohols or

thioalcohols. In this way, a urethane macromonomer is obtained which has lateral and terminal vinyl groups.

5 Urethane macromonomers that have only terminal vinyl groups are obtained by reacting polyhydroxy compounds (A), polyhydroxy acids (D) and/or polyamino or polymercapto acids (D') and the monomers (C1), having a group which is reactive toward isocyanate and a vinyl group, with the polyisocyanates (B). In the polyaddition reaction, the monomers (C1) act as chain terminators. These urethane macromonomers also can be prepared in a plurality of reaction steps, for example, by reacting an isocyanato-terminal urethane macromonomer which is free from vinyl groups and which is composed of the units (A), (B) and (D) and/or (D') with monomers (C1).

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A fifth method of preparation entails subsequent incorporation of the polyhydroxy acids (D) into the previously-formed urethane macromonomer that contains isocyanate end groups. In this method the first step is reaction of a mixture of the polyhydroxy compounds (A) with the polyisocyanates (B) and with the vinyl monomers (C) which are reactive toward isocyanate, the quantities employed being selected so that macromonomers that have isocyanate end groups are obtained. In the following step these products are reacted with the polyhydroxy acids (D) or with the polyamines or polythiols (D') which contain acid groups.

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A preferred procedure is not to incorporate the dihydroxyvinyl compound during the polyaddition, at the same time as the polyol, but instead first to

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react a prepolymer composed solely of polyol, polyisocyanate and, if desired, polyhydroxy acid to give an OH- or NCO-terminal prepolymer. In a second step this prepolymer is then reacted with the dihydroxyvinyl compound and further polyisocyanate to give the vinyl-containing, OH- or NCO-terminal macromonomer.

In this reaction, the proportions are chosen so that the polyisocyanate is in excess, in which case the prepolymer formed contains not only carboxyl, phosphono and/or sulfo groups, but also free isocyanate groups. A preferred procedure is initially to employ the polyisocyanate in excess, in order to obtain a prepolymer containing free hydroxyl groups. In an additional step this prepolymer is then reacted with further polyisocyanate, in order likewise to obtain a prepolymer that contains free isocyanate groups.

The macromonomers obtained by these various routes are then neutralized, unless the acid groups in the monomers that carry such groups were employed in neutralized form from the start. Neutralization is carried out with aqueous solutions of alkali metal hydroxides or with amines, for example, with trimethylamine, triethylamine, dimethylaniline, diethylaniline, triphenylamine, dimethylethanolamine, aminomethylpropanol, dimethylaminomethylpropanol, dimethylisopropanolamine or with ammonia. Neutralization also can be undertaken with mixtures of amines and ammonia.

In order to prepare the polyurethane dispersions (b), macromonomers that contain vinyl groups are transferred by addition of water to an



aqueous dispersion and are polymerized using methods known per se by means of free-radical initiator systems. In this polymerization it is possible to incorporate monomers of this kind as described above, if not present from the start in the form of so-called reactive diluents (E), by polymerization into the polyurethane. It is also possible to add carboxyl-, hydroxy-, amino-, ether- and mercapto-functional  $\alpha,\beta$ -unsaturated vinyl monomers directly before or during the free-radical polymerization. Examples of such monomers include hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, (meth)acrylic acid, crotonic acid, glycidyl methacrylate, t-butylaminoethyl methacrylate or dimethylaminoethyl methacrylate. The content of copolymerized vinyl monomers preferably is from 0 to 95% by weight, preferably from 5 to 70% by weight, based on the solids content of the polyurethane dispersion. The ratio of soft to hard segments in the polyurethane macromonomers preferably is from 0.30 to 6, particularly preferably from 0.8 to 3. Suitable initiators for the polymerization include known free-radical initiators, such as ammonium peroxodisulfate, potassium peroxodisulfate, sodium peroxodisulfate, hydrogen peroxide, organic peroxides such as cumene hydroperoxide, t-butyl hydroperoxide, di-tert-butyl peroxide, dioctyl peroxide, tert-butyl perpivalate, tert-butyl perisononanoate, tert-butyl perethylhexanoate, tert-butyl perneodecanoate, di-2-ethylhexyl peroxodicarbonate and diisotridecyl peroxodicarbonate, and also azo compounds such as azobis(isobutyronitrile), azobis(4-cyanovaleric

acid), or the customary redox systems, for example, sodium sulfite, sodium dithionite, ascorbic acid and organic peroxides or hydrogen peroxide, if desired in conjunction with accelerators such as iron salts or cerium salts. It is also possible to add regulators (thiols), emulsifiers, protective colloids and other conventional auxiliaries.

If the preparation of the macromonomer was carried out in a solvent which can be removed by distillation and which forms an azeotrope with water or can be removed by fractionation from the aqueous phase, for example, in acetone, dioxane, methyl ethyl ketone, methyl isobutyl ketone, tetrahydrofuran, toluene or xylene, then this solvent is removed from the dispersion by distillation. In every case an aqueous polyurethane dispersion is obtained.

The acid numbers of these polyurethanes preferably are within the range from 5 to 80, particularly preferably in the range from 10 to 40, mg of KOH per g of solid resin. The hydroxyl numbers of these polyurethanes preferably are within the range from 5 to 150, and more preferably from 10 to 120, mg of KOH per g of solid resin.

Further details on the preparation of the macromonomers and their polymerization to give the polyurethane dispersions according to the invention are evident from the following general process descriptions. These process conditions represent preferred embodiments. In addition, all documents mentioned in this application are incorporated by reference herein in their entirety.

1. Solvent-free polyurethane dispersion

a. produced without auxiliary solvents

At temperatures of from 100 to 150°C, preferably from 120 to 135°C, the polyhydroxy acid (D) and, if desired, low molecular weight polyols (A4) are dissolved in a polyol (A) having an average molecular weight of from 400 to 5000 and are reacted with a polyisocyanate (B) or a mixture of polyisocyanates to give an OH-terminal product that has an average molar mass (Mn) of from 500 to 12,000, particularly preferably from 600 to 8000. After the reaction mixture has been cooled to a temperature of from 30 to 100°C, preferably from 50 to 80°C, a vinyl monomer (E) which is not isocyanate-reactive is added. Further polyisocyanate is added at this temperature to produce an NCO-terminal resin which is subsequently reacted with an NCO-reactive vinyl compound (C1 and/or C2) to give a polyurethane macromonomer having an average molar mass of from 700 to 24,000, preferably from 800 to 16,000, g/mol. If desired, amines, alcohols or thiols are also added at this point, which react with any isocyanate groups still present to form terminal urea, urethane or thiourethane groups. The resin solution obtained in this way is neutralized with amines or other bases and then dispersed in water. Further vinyl comonomers (E) can be added to the resulting dispersion before or during the free-radical polymerization which follows. The free vinyl compound is then polymerized in the aqueous dispersion using free-radical initiators at a temperature of from 0 to 95°C, preferably from 40 to 95°C, or at a temperature of from 30 to 85°C if

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redox systems are used. This produces a solvent-free polyurethane dispersion.

**b. produced with auxiliary solvent**

5 In contrast to method 1.a., in this case all  
of the polyol components (A), (D) are dissolved in  
a solvent which can be fractionated from the aqueous  
phase or which forms an azeotrope with water, and  
are reacted directly with polyisocyanate (B) or  
10 mixtures of polyisocyanates to give the NCO-terminal  
product. The content of solvent is between 1 and  
80% by weight, preferably between 10 and 50% by  
weight, based on the solids content of the  
polyurethane macromonomer. The temperature for this  
15 step is between 30 and 100°C, preferably between 50  
and 80°C. After the reaction with an isocyanate-  
reactive vinyl compound (C1 and/or C2) to give a  
polyurethane macromonomer that has a molar mass of  
from 500 to 30,000, preferably from 700 to 20,000,  
g/mol, amines, alcohols or thiols are added, if  
20 desired, which react with any isocyanate groups  
still present to form terminal urea, urethane or  
thiourethane groups. The resin solution obtained in  
this way is neutralized with amines or other bases  
and then dispersed in water. The auxiliary solvent  
25 is subsequently distilled off from the aqueous  
phase, possibly under a slight vacuum. Vinyl  
comonomers (E) can be added to this solvent-free  
dispersion before or during the free-radical  
polymerization which follows. Polymerization is  
30 subsequently carried out with free-radical  
initiators at a temperature of between 0 and 95°C,  
particularly preferably between 40 and 95°C, or

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using Redox systems at a temperature of between 30 and 85°C, to give a solvent-free polyurethane dispersion.

## 2. Solvent-containing polyurethane dispersion

5           When a non-distillable auxiliary solvent such as N-methylpyrrolidone is used, the procedure is exactly as in method 1.b. except that distillation after the dispersion is omitted and, if desired, vinyl monomers (E) can be added before or during the  
10       free-radical polymerization. The polymerization is carried out as in method 1.b. The content of solvent is in the range from 0.1 to 30% by weight, particularly preferably from 1 to 15% by weight, based on the overall binder dispersion.

15           The content of polyurethane resin (b) (calculated as solids) in the aqueous coating composition is generally from 5 to 40% by weight, preferably from 15 to 30% by weight, based on the overall coating composition.

20           In addition to the polyurethane resin, the aqueous coating composition also may contain, as a binder, up to 60% by weight, preferably up to 30% by weight, based on the polyurethane resin, of other oligomeric or polymeric materials, such as water-  
25       soluble or water-dispersible phenolic resins, polyester resins, epoxy resins, melamine resins or acrylic resins, etc., as described, for example, in EP-A 089 497.

30           In order to prepare a ready-to-use coating compositions the polyisocyanate component (a) is emulsified in the aqueous dispersion/solution of the polyurethane resin (b), the dissolved or dispersed

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polyurethane resin taking on the function of an emulsifier for the added polyisocyanate (a).

5           Mixing can be effected simply by stirring at room temperature. Preferably, however, a suitable apparatus is used in order to achieve very highly homogenous mixing of components (a) and (b), examples of such apparatus being high-speed stirrers or high-speed dispersion units. Also suitable are the units known to those skilled in the art for two-  
10           component application, in which both components are mixed by means of appropriate mixing chambers shortly before application. In this case the quantity of the polyisocyanate component is calculated so as to result in a ratio of NCO/OH  
15           equivalents, based on the isocyanate groups of component (a) and the alcoholic hydroxyl groups of component (b), of from 0.5:1 to 5:1, preferably from 0.8:1 to 4:1.

          Prior to the addition of the polyisocyanate  
20           component (a) it is possible to incorporate the conventional auxiliaries and additives of paint technology into the polyurethane resin dispersion (b) of the polymers. Examples of such auxiliaries and additives include antifoams, leveling agents,  
25           slip agents, wetting agents, dispersion auxiliaries, organic and inorganic fillers and pigments, organic and inorganic acids and bases, protective colloids, emulsifiers, preservatives, etc.

          The coating compositions according to the  
30           invention which are obtained in this way are suitable for virtually all applications in which solvent-containing, solvent-free or other kinds of aqueous paint or coating systems having an improved

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profile of properties are desired. The substrates to be coated include, for example, metal, such as iron and also nonferrous metals, mineral materials such as lime, cement or plaster, fiber-cement building materials, concrete, wood or wood materials, paper, asphalt, bitumen, plastics of various kinds, composite materials, glass, ceramic, textiles or leather. The metallic substrates are preferably automobiles and rail-bound vehicles. The coating compositions according to the invention are, for example, sealers, primers, fillers or pigmented or transparent topcoats and/or clearcoats.

The coating compositions according to the invention can be applied by any methods known to those skilled in the art, for example, by brushing, rolling, flow-coating, knife-coating, dipping and, in particular, by spraying. It is possible to employ a very wide variety of spraying methods, such as pressurized-air spraying, airless, air-mix or electrostatic spraying and using 1- or 2-component spraying units.

The drying and/or curing of the binder combinations according to the invention or of the coatings based thereon is/are carried out for a sufficiently long time at temperatures of 10 - 250°C, preferably 10 - 100°C.

The invention is illustrated in more detail by the examples given below:

**Example 1:**

An amount of 252.0 g of a polyester prepared from 1,6-hexanediol, isophthalic acid, adipic acid and dodecenylsuccinic anhydride and having a

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hydroxyl number of 84 and an acid number of less than 2, together with 50.2 g of dimethylolpropionic acid, are heated to 130°C and maintained at this temperature until a homogenous solution is obtained.

5 Subsequently 106.0 g of tetramethylxylylene diisocyanate are metered in with stirring over a period of from 20 to 25 minutes and stirring is continued at 130°C until no further free isocyanate groups are present. After the mixture has been

10 cooled to 70°C, 2.5 g of 1,4-butanediol, 11.8 g of glycerol methacrylate, 131.3 g of methylmethacrylate and 0.3 g of 2,6-di-tert-butyl-4-methylphenol are quickly added and the mixture is homogenized. Thereafter 81.6 g of tetramethylxylylene

15 diisocyanate are metered in over a period of 20 minutes and the mixture is reacted at 70°C until the content of free isocyanate groups is 1.39% by weight, based on the weight of all the components. Diethanolamine (21.6 g) is added quickly to the

20 resulting prepolymer solution, which is homogenized for 10 minutes. Following the metered addition of 28.4 g of triethylamine, 15.9 g of methyl methacrylate at 28.0 g of 2-hydroxyethyl methacrylate, 1087.6 g of water at a temperature of

25 70°C are added to the prepolymer solution with intensive stirring. The temperature subsequently is raised to 80°C and 0.7 g of tert-butyl hydroperoxide (80% strength in di-tert-butyl peroxide) are quickly added dropwise. After a further 30 minutes a

30 solution of 1.3 g of ascorbic acid in 130 g of water is metered in over a period of 90 minutes. The temperature is maintained at 80°C for a further hour.



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The resulting polyurethane-acrylic hybrid dispersion is cooled to room temperature and filtered through a 5  $\mu$ m filter cloth. The dispersion has a solids content of 36% and a pH of 7.0.

**Example 2:**

An amount of 252.0 g of a polyester prepared from 1,6-hexanediol, isophthalic acid, adipic acid and dodecenylsuccinic anhydride and having a hydroxyl number of 84 and an acid number of below 2, together with 50.2 g of dimethylolpropionic acid, are heated to 130°C and maintained at this temperature until a homogenous solution is obtained. Subsequently 106.0 g of tetramethylxylylene diisocyanate are metered in with stirring over a period of from 20 to 25 minutes and stirring is continued at 130°C until no further free isocyanate groups are present. After the mixture has been cooled to 70°C, 2.5 g of 1,4-butanediol, 11.8 g of glycerol methacrylate, 131.3 g of methylmethacrylate and 0.3 g of 2,6-di-tert-butyl-4-methylphenol are quickly added and the mixture is homogenized. Thereafter 81.6 g of tetramethylxylylene diisocyanate are metered in over a period of 20 minutes and the mixture is reacted at 70°C until the content of free isocyanate groups is 1.39% by weight, based on the weight of all the components. Diethanolamine (21.6 g) is added quickly to the resulting prepolymer solution, and the mixture is homogenized for 10 minutes. Following the metered addition of 28.4 g of triethylamine, 22.9 g of methyl methacrylate, 7.0 g of methacrylic acid and

14.0 g of 2-hydroxyethyl methacrylate, 1087.6 g of water at a temperature of 70°C are added to the prepolymer solution with intensive stirring. The temperature is subsequently raised to 80°C and 0.7 g of tert-butyl hydroperoxide (80% strength in di-tert-butyl peroxide) are quickly added dropwise. After a further 30 minutes a solution of 1.3 g of ascorbic acid in 130 g of water is metered in over a period of 90 minutes. The temperature is maintained at 80°C for a further hour.

The resulting polyurethane-acrylic hybrid dispersion is cooled to room temperature and filtered through a 5  $\mu$ m filter cloth. The dispersion has a solids content of 36% and a pH of 6.7.

#### Example 3:

An amount of 261.0 g of a polyester prepared from neopentyl glycol, 1,6-hexanediol, isophthalic acid and adipic acid and having a hydroxyl number of 41 and an acid number of less than 2, with 43.0 g of dimethylolpropionic acid, 3.5 g of 1,6-hexanediol and 120.5 g of N-methyl-2-pyrrolidone, are heated to 80°C. Subsequently 119.1 g of isophorone diisocyanate are metered in with stirring over a period of from 25 to 30 minutes and the mixture is stirred at 80°C until the content of free isocyanate groups is 1.38% by weight, based on the total weight of all the components. 2-hydroxyethyl methacrylate (23.4 g) and 0.2 g of 2,6-di-tert-butyl-4-methylphenol are added to the resulting prepolymer solution. Reaction is carried out until there are no more free isocyanate groups present. After

addition of 99.7 g of methyl methacrylate, 33.2 g of 2-ethylhexyl acrylate and 60.0 g of 2-hydroxyethyl methacrylate and following a 5-minute homogenization phase, the mixture is neutralized with 24.4 g of triethylamine. Water (1091.8 g) at a temperature of 75°C is then added to the prepolymer solution with intensive stirring. Subsequently, at a temperature of 80°C, 0.7 g of tert-butyl hydroperoxide (80% strength in di-tert-butyl peroxide) are quickly added dropwise. After a further 30 minutes a solution of 1.3 g of ascorbic acid in 130.0 g of water is metered in over a period of 90 minutes.

The resulting polyurethane-acrylic hybrid dispersion is cooled to room temperature and filtered through a 5  $\mu$ m filter cloth. The dispersion has a solids content of 32% and a Ph of 7.1.

Acrylic polyurethane dispersions prepared in accordance with Examples 1 to 3, in combination with a commercial polyisocyanate curing agent (Desmodur® VPLS 2032 from Bayer AG, a water-emulsifiable aliphatic polyisocyanate based on hexamethylene diisocyanate), were tested with regard to their properties in a clear coat formulation. The comparison substance used was a commercial, nonacrylic OH-functional polyurethane dispersion (Daotan® VTW 1225 from Hoechst AG).

#### Application Example 1.1:

One part by weight of a commercial levelling agent (Additol® XW 390 from Hoechst AG), 5 parts by weight of butyl glycol and 3.5 parts by weight of

deionized water are added with thorough stirring to 80.5 parts by weight of a polyurethane dispersion according to Example 1. Shortly before application the batch is mixed with the curing agent solution, comprising 14.5 parts by weight of Desmodur® VPLS 2032, 2.5 parts by weight of butyl acetate and 0.9 part by weight of white spirit, using a high-speed stirrer, and is then ready for application.

**Application Example 2.1:**

One part by weight of a commercial levelling agent (Additol® XW 390 from Hoechst AG), 5 parts by weight of butyl glycol and 3.5 parts by weight of deionized water are added with thorough stirring to 80.5 parts by weight of a polyurethane dispersion according to Example 2. Shortly before application the batch is mixed with the curing agent solution, comprising 14.5 parts by weight of Desmodur® VPLS 2032, 2.5 parts by weight of butyl acetate and 0.9 part by weight of white spirit, using a high-speed stirrer, and is then ready for application.

**Application Example 3.1:**

One part by weight of a commercial levelling agent (Additol® XW 390 from Hoechst AG), 5 parts by weight of butyl glycol and 3.5 parts by weight of deionized water are added with thorough stirring to 80.5 parts by weight of a polyurethane dispersion according to Example 3. Shortly before application the batch is mixed with the curing agent solution, comprising 12.9 parts by weight of Desmodur® VPLS 2032, 2.2 parts by weight of butyl acetate and 0.8

part by weight of white spirit, using a high-speed stirrer, and is then ready for application.

**Comparative application example:**

5           One part by weight of a commercial levelling agent (Additol® XW 390 from Hoechst AG), 5.2 parts by weight of butyl acetate and 5.6 parts by weight of deionized water are added with thorough stirring to 86.2 parts by weight of the OH-functional, nonacrylic polyurethane dispersion Daotan® VTW 1225 (Hoechst AG).  
10           Shortly before application the batch is mixed with the curing agent solution, comprising 17.3 parts by weight of Desmodur® VPLS 2032, 3.3 parts by weight of butyl acetate and 1.1 parts by weight of white spirit, using a high-speed stirrer,  
15           and is then ready for application.

          The finished clearcoat formulations were applied to glass panels and polycarbonate panels, respectively, at a wet-film thickness of 150  $\mu\text{m}$  (corresponding to a dry-film thickness of  
20           approximately 30 to 40  $\mu\text{m}$ ), and the panels were flashed off at room temperature for 10 min and then dried at 80°C for 30 min and then at 60°C for 16 h.

          After the coatings had cooled, the following properties were tested (results are given in Table  
25           1):

- general appearance of the coating, by subjective assessment
- adhesion to the substrate with crosshatch in accordance with DIN 53 151

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- pendulum hardness according to König, in accordance with DIN 53 157
  - resistance to selected solvents (columns 6 through 10), the value given being the period of action after which the coatings are soft and no longer scratch-resistant
  - resistance to selected chemicals (columns 11 and 12), the period of action being 16 h; the following evaluation scale was used:
    - satisfactory = no attack
    - largely satisfactory = slight attack but coating still intact
    - not satisfactory = coating very heavily attacked or completely destroyed.
- 5
- 10
- 15

TABLE 1

Appli- cation Example	Appear- ance	Adhe- sion to glass	Adhe- sion to poly- carbon- ate	Pendulum hardness	Isopro- panol	Isopro- panol/ water 1:1	Ethanol water 1:1	Resistance to: Ethanol Ethanol/ water 1:1	FAM** super (pre- mium- gasol- ine	Tar	5% sodium hydr- oxide solu- tion
1.1	Clear, smooth, no cracks	Gt 0	Gt 0	80 s	20 min	15 min	4 min	10 min	1 min	largely sat. sat. *	
1.2	Clear, smooth, no cracks	Gt 0	Gt 0	100 s	5 min	5 min	2 min	5 min	1 min	largely sat. sat. *	
1.3	Clear, smooth, no cracks	Gt 0	Gt 0	147 s	20 min	10 min	4 min	8 min	>30min	largely sat. sat. *	
Compa- rative	Clear, smooth, no cracks	Gt 0	Gt 0	90 s	10 min	10 min	3 min	5 min	7 min	not sat.	not sat.
Col.1	2	3	4	5	6	7	8	9	10	11	12

\* pale yellow discoloration.

[German Technical Committee on standardization of mineral oil and fuels]

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What is claimed is:

1. A water-dilutable, two-component coating composition comprising:

- 5 (a) a polyisocyanate component that contains at least one organic polyisocyanate, and
- (b) an aqueous polyurethane dispersion prepared by radical-initiated polymerization of polyurethane macromonomers that contain:
- 10 - at least one carboxyl, phosphono or sulfo group,
- at least one vinyl group, which group may be a lateral group or a
- 15 terminal group, and
- optionally at least one hydroxyl, urethane, thiourethane or urea group.

2. A coating composition as claimed in claim 1, wherein the aqueous polyurethane dispersion (b) is prepared by:

20

producing a urethane macromonomer by radical-initiated polymerization of:

- (A) one or more polyhydroxy compounds selected from the group consisting of:
- 25 (A1) polyhydroxy-polyethers,
- (A2) polyhydroxy-polyesters, and
- (A3) polyhydroxy-polycarbonates, and, optionally
- (A4) low molecular weight compounds
- 30 possessing two or more functional groups selected in each case from



among hydroxyl, amino and  
mercapto groups,

(B) one or more polyisocyanates,

(C) one or more vinyl monomers that  
contain at least one vinyl group,  
selected from the group consisting of:

(C1) vinyl monomers that contain one  
group which is reactive toward  
isocyanate groups, which group is  
selected from an amino, hydroxyl  
and mercapto group,

(C2) vinyl monomers that contain at  
least two groups which are  
reactive toward isocyanate  
groups, selected as defined in  
(C1),

it being possible for the vinyl  
monomers (C1) and (C2), if desired, to  
be employed in a mixture,

(D) polyhydroxy compounds that contain at  
least one acid group selected from a  
carboxyl, sulfo and phosphono group,  
and, optionally,

(D') acid-group-containing polyamines,  
polythiols or amino alcohols or amino  
thiols, the acid groups of which are  
as defined in (D), and

reacting the urethane macromonomer with at least  
one alcohol, amine or thiol,

wherein the resulting polyurethane contains acid  
groups, terminal hydroxyl groups and vinyl groups,

which vinyl groups may be terminal or lateral vinyl groups.

3. A water-dilutable, two-component coating composition as claimed in claim 1, wherein the urethane macromonomer is prepared in the presence of a vinyl compound (E) or in the presence of a mixture of two or more vinyl compounds (E), the vinyl compounds (E) being selected from the group consisting of:

- 10                   - esters of olefinically unsaturated mono- or polycarboxylic acids with mono- or polyhydric (cyclo)aliphatic, aromatic or mixed aliphatic-aromatic alcohols having 1 to 15 carbon atoms,
- 15                   - amides or nitriles of the above-defined carboxylic acids, which in the case of the amides optionally may be substituted on the nitrogen atom,
- 20                   - esters of mono- or polyhydric, olefinically-unsaturated alcohols with (cyclo)aliphatic, aromatic or mixed aliphatic-aromatic carboxylic acids that have 2 to 15 carbon atoms,
- 25                   - olefinically-unsaturated aldehydes and ketones,
- ethers of mono- or polyhydric, olefinically-unsaturated alcohols with (cyclo)aliphatic, aromatic or mixed aliphatic-aromatic alcohols that have
- 30                   1 to 15 carbon atoms,
- vinyl and vinylidene halides, and
- vinyl aromatic compounds.

4. A coating composition as claimed in claim 1, wherein the aqueous polyurethane dispersion (b) is prepared by radical-initiated polymerization in a mixture of water and an organic solvent which is inert toward isocyanate groups, optionally in the presence of unsaturated monomers (E) which are copolymerizable with the polyurethane macromonomers, and optionally with removal of the organic solvent by distillation before or after the free-radical polymerization.

5. A coating composition as claimed in claim 1, wherein the aqueous polyurethane dispersion (b) is prepared by radical-initiated polymerization in an unsaturated monomer (E) which serves as solvent and is copolymerizable with the polyurethane macromonomers, optionally in the presence of further copolymerizable unsaturated monomers (E).

6. A water-dilutable two-component coating composition as claimed in claim 1, wherein the polyisocyanate component a) has an average NCO functionality of between 2 and 5.

7. A water-dilutable two-component coating composition as claimed in claim 1, wherein the polyisocyanate component a) consists of one or more polyisocyanates, the free isocyanate groups of which are attached to aliphatic structures.

8. A water-dilutable two-component coating composition as claimed in claim 1, wherein the polyisocyanate component a) comprises

derivatives of diisocyanates containing groups selected from biuret, urethane, uretdione, and isocyanurate groups.

5           9.    A water-dilutable two-component coating composition as claimed in claim 1, wherein the polyisocyanate component a) comprises hexamethylene diisocyanate and its derivatives.

10          10.   A water-dilutable two-component coating composition as claimed in claim 1, wherein the component (A) is based on a polyhydroxy polyester.

15          11.   A water-dilutable two-component coating composition as claimed in claim 1, wherein the component (A) is a mixture of a polyhydroxy polyester and a low molecular weight compound with two or more functional groups selected from hydroxyl, amino and mercapto groups.

20          12.   A water-dilutable two-component coating composition as claimed in claim 1, wherein the component (C) comprises monomers with one vinyl group and at least two hydroxy groups.

25          13.   A water-dilutable two-component coating composition as claimed in claim 1, wherein the component (D) comprises compounds with two hydroxy groups and one group selected from carboxylic, sulphonic, and phosphonic acid groups.

14.   A water-dilutable two-component coating composition as claimed in claim 1, wherein

the component (E) is selected from alkyl acrylates and methacrylates with 1 to 20 carbon atoms in the alkyl groups.

5           15. A process for the preparation of a water-dilutable two-component coating composition as claimed in claim 2, wherein prior to the polymerization of the urethane macromonomers, at least one vinyl monomer is added which carries at least one functional group selected from the group  
10           consisting of carboxyl, hydroxyl, amino, ether and mercapto groups.

          16. The process as claimed in claim 15, wherein the unsaturated monomer (E) is added before or during polymerization but after the  
15           synthesis of the urethane macromonomer.

          17. A method of coating, comprising the steps of:  
                    providing a substrate, and  
                    coating a layer of a composition as  
20           claimed in claim 1 on the substrate.

          18. The method as claimed in claim 17, wherein the substrate is a metallic substrate.